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L4: Entry 3 of 7 File: USPT

DOCUMENT-IDENTIFIER: US 5389433 A
TITLE: Battery separator

Brief Summary Text (3):
Membranes have been formed from various materials and used in various applications such as in ion exchange, osmotic and ultra filtration devices including desalinization, kidney dialysis, gas separation and other applications. Macro and microporous membranes have been used as a means of insulating and separating electrodes in battery devices. Each application provides an environment and a set of desired parameters which are distinct to the specific application.

Brief Summary Text (5):
It is generally agreed that one of the critical elements in a battery design is the separator component and, to be highly effective in the design, the separator should have a combination of features. The battery separator must be resistant to degradation and instability with respect to the battery environment, including the other battery components and the battery chemistry. Thus, the battery separator must be capable of withstanding degradation of strong acids (such as sulfuric acid commonly used in acid battery designs) or strong alkali (such as potassium hydroxide used in alkaline battery designs) and to do so under ambient and elevated temperature conditions. Further, the separator should also be of a thin and highly porous character to provide a battery of high energy density. Although battery separators of thick or heavy design have been utilized in the past, such materials detract from the overall energy density of the battery by reducing the amount of electrodes that can be contained in a predetermined battery configuration and size. Another criteria is that the battery separator must be capable of allowing a high degree of electrolytic conductivity. Stated another way an effective separator membrane must exhibit a low electrical resistance when in the battery. The lower the electrical resistance the better the overall battery performance will be. A still further criteria is that the separator should be capable of inhibiting formation and growth of dendrites. Such dendrite formation occurs during battery operation when part of the electrode material becomes dissolved in the electrolyte and, while passing through the separator, deposits therein to develop a formation which can, after a period of time, bridge the thickness of the separator membrane and cause shorting between electrodes of opposite polarity.

Brief Summary Text (7):
Various microporous membranes or sheet materials have been suggested for utilization as a battery separator. Separators conventionally used in present battery systems are formed of polymeric films which when placed in an electrolyte or an electrolyte system, are capable of exhibiting a high degree of conductivity while being stable to the environment presented by the battery system. The films include macroporous as well as microporous materials. The porosity permits transportation of the electrolyte. Examples of such separators include unfilled polyolefin sheets which have been stretched and annealed to provide microporosity to the sheet, such as is described in U.S. Pat. Nos. 3,558,764; 3,679,538; and 3,853,601. In addition, polyolefin separators which include filler materials are disclosed in U.S. Pat. Nos. 3,351,495 and 4,024,323. In general, such polymer/filler compositions are friable materials and tend to exhibit electrical resistance which does not permit the formation of a highly efficient, high energy battery system.

Brief Summary Text (8):
Polysulfones are a known class of polymers which have been used to form various types of membranes. Polysulfone membranes are of a substantially non-flexible physical form. They have been widely used in forming in various separation apparatus, such as osmotic and ultrafiltration devices. Separation membranes differ from and do not normally have

the constraints such as described in U.S. Pat. Nos. 3,855,122 and 3,709,841 placed upon a battery separator. For example, separation membranes are normally anisotropic in configuration (that is, asymmetrical in surface configuration, are not required to be ultra thin, and do not have to provide a high void volume as desired for battery separator designs. Further, such separation membranes are not conventionally used in highly corrosive environments as is conventionally found in a battery nor do they undergo the high degree of handling and processing as is required in the assembly of a battery. It has been noted that U.S. Pat. No. 4,714,663 discloses the use of a cast polysulfone membrane which is free of tertiary hydrogen atoms as being useful in a zinc ferricyanide battery, as an ion-selective separation membrane. The polysulfone separator is used as a means for separating the two different electrolyte solutions of this particular battery design.

Brief Summary Text (18):
A "separator" is a component of a battery which provides a means of separation between adjacent electrode plates or members of opposite polarity. The separator of the present invention may have various configurations, such as a flat or ribbed material in the form of a membrane or envelope design capable of maintaining separation between electrodes.

Brief Summary Text (20):
A "polysulfone", "polyarylsulfone", "polyether sulfone" and "polyarylether sulfone" are each intended to define a polymeric material having a combination of sulfone groups, aryl groups and ether groups in the polymer chain and which may also contain alkylene groups therein.

Brief Summary Text (24):
The polymer used to form the body of the sheet product of the present invention should be a polysulfone. This class of polymers has been known to be substantially inert with respect to acid and alkali conditions and, as discussed above, has been formed into separation membranes for numerous applications. The previously known membranes have been thick, brittle and susceptible to cracking and forming other imperfections or, if thin, have been weak and required delicate handling and use. The present invention is directed to a unique sheet product which forms the acid and alkali resistant polysulfone into a microporous sheet product capable of exhibiting the combination of properties described hereinabove which are needed to form a desired battery separator for acid or alkaline design.

Brief Summary Text (27):
where in this reaction Ar and/or Ar' groups contain the sulfone entity. As an example a polysulfone is formed by the condensation of 4,4-dichlorodiphenyl sulfone with an alkali metal salt of Bisphenol A. The subject polysulfones are commercially available under the tradenames of Udel (Amoco); Astrel (3M); Victrex (ICI), and Radel (Amoco).

Brief Summary Text (53):
Although it is common practice to form membranes with the aid of a support member, it is preferred herein that the support sheet should be impregnated with the liquid dope composition by applying the dope onto one major surface of the support sheet and forcing it through the sheet while maintaining the other major surface free. As stated above, a second application of dope composition (preferably of higher viscosity) may be applied to one or both surfaces. This mode of application is preferred when applying a low filler content dope composition. The impregnated sheet may then be processed through a means for regulating its thickness such as by using doctor blades or the like and subsequently immersed into a bath of second liquid in a manner which substantially simultaneously contacts each of the major surfaces of the impregnated sheet to second liquid. The second liquid should not be allowed to accumulate high concentrations of first liquid therein. All of these steps are done without the aid of a support member, as is common practice. After the impregnated sheet has been contacted with the second liquid to cause the polymer to set, the resultant sheet product may be brought into contact with directional rollers and the like. The resultant sheet product should be washed with fresh amounts of second liquid to cause removal of the first liquid material. For example, when the first liquid is selected from a polar solvent such as N-methyl pyrrolidone, the amine solvent should be substantially completely removed.

Brief Summary Text (54):
The resultant sheet product is a microporous sheet of very high porosity (porosity of 50 vol. percent and even up to 80 vol. percent). The sheet product has a length and breadth and a predetermined thickness which should be less than about 50 mils, preferably less than about 20 mils, and most preferably less than about 10 mils. Very

thin, flexible sheet products having good mechanical properties of tensile strength and modulus of elasticity have been unexpectedly formed. It is well known that polysulfone membranes have very poor mechanical properties, especially in flexibility and flexural strength, and that the inclusion of high levels of particulate filler into the polysulfone matrix would presumably further cause the sheet product to have increased brittle characteristics while the high porosity would be presumed to cause a sheet product of very low tensile strength and poor integrity. Instead, it has been unexpectedly found that the sheet product of this invention provides all of the desired properties for a battery separator including strength, flexibility, very low electrical resistance, good integrity, etc.

Detailed Description Text (2):
A solution was prepared by mixing 4.7 parts of a polyarylether sulfone formed from Bisphenol-A and dichlorodiphenyl sulfone (Amaco, Udel P-1835), 4.7 parts precipitated silica (Davison, Sylox-2), 0.06 part 2,2-diethyldihexylamine, 0.15 part polyacrylic acid and 48.9 parts N-methylpyrrolidone using a high shear mixer (Myers). The solution had a viscosity of 8.93.times.10.sup.3 cps (Brookfield viscometer with #3 spindle at 12 rpm).

Detailed Description Text (6):
A separator product was formed in the same manner as described in Example I (1) above except that the polymer/filler solution was formed from 48 parts polyarylether sulfone (Udel), 48 parts talc, 0.5 part DEDHA, 1.5 parts polyacrylic acid and 504 parts N-methylpyrrolidone. The solution had a viscosity of 2.02.times.10.sup.3 cps (Brookfield, #3 spindle, 12 rpm). The nonwoven web was heavier (0.6 oz/sq. yd.). The formed separator exhibited a total void volume of 58 percent, a morphology of very small pores at the surface which gradually developed into larger pores internally and the web was internal in the separator product. The separator showed an ER of 0.87 ohm-cm.

Detailed Description Text (9):
In all cases the sheet product exhibited good flexibility and very low electrical resistance. The product did not exhibit flaking or disintegration of the product which is conventionally observed with highly filled polymeric membranes.

Detailed Description Text (12):
A dope was prepared by dispersing 1 part of precipitated silica (Sylox-2) and 1 part polyarylether sulfone (Amaco-Udel P-1700) in 7.3 parts N-methyl pyrollidone (NMP) using a high speed disperser/mixer. While maintaining the mixture at less than 30.degree. C., 0.03 part of di(2-ethylhexyl)amine (DEHA) in 2.6 part NMP was mixed in at low speed followed by 0.03 part of a polyacrylic acid of MW.sub.4 =4,000,000 (Carbopol 940) in 1.9 parts NMP. The resultant mixture had a viscosity of 3300 cps (Brookfield, #4 at 50 rpm).

Detailed Description Text (14):
A 9 inch wide polyester, non-woven sheet of 0.75 oz/yd.sup.2 (Reemay 2275, Reemay, Inc.) was saturated by passing it continuously through a bath of the above 950 cP solution with the excess swept off using a Delrin bar riding on top of saturated web. The sheet was then coated with 3300 cP solution using a knife blade set at 14 mil over a stainless steel smooth surface. The dual coated fabric was directed 45 degrees off of the plate and into a water coagulation bath (<35% N-methyl pyrrolidone in water) at a speed between 3 and 8 feet per minute. The coagulated material was completely formed within 10 seconds of immersion in the room temperature bath. The residence time in this bath was about 90 seconds. The product was then passed through a D.I. water rinse bath (residence time of 120 seconds), a spray wash zone (2 gpm water spray) and take up. The membrane was dried on a steam drum at 80.degree. to 95.degree. C. The sheet product was 7.5-8.5 mil thick, had a porosity from 70 to 73%, showed a maximum pore size of 0.7 to 1.5 micron, an average pore size of 0.1 to 0.12 micron, and has an electrical resistance of 3.5 to 4.5 mohn-in.sup.2.

Detailed Description Text (19):
A separator useful for alkaline battery system was prepared from an unfilled sheet product. The sheet product was achieved by initially mixing 1 part polyarylether sulfone (Amaco-Udel P-1700) in 9.0 parts of N-methyl pyrollidone (NMP) using a high speed disperser/mixer. While maintaining the mixture at less than 30.degree. C., 5 parts of a polyacrylic acid of MW.sub.w =4,000,000 (Carbopol 940) in NMP as 1% solution was added to the mixer followed by 10 parts of 2,2-diethyldihexylamine. The resultant mixture had a viscosity of 150 cps (Brookfield viscometer with #3 spindle at 12 rpn).

Detailed Description Text (22):
A separator useful for alkaline battery systems was produced in a similar manner to that described in Example VI above except that the dope was formed from a mixture of 8.4 parts NMP, 0.8 part polysulfone (Udel P-1700), 0.8 part powder Tio.sub.2, 5 parts Carbopol 940 and 10 parts of 2,2-diethyldihexylamine. The viscosity of the resultant dope was 150 cps (Brookfield viscometer with #3 spindle at 12 rpm).

CLAIMS:

4. The battery separator of claim 1, 2, or 3 wherein the polyether sulfone component of said sheet product is a polyaryl ether sulfone homopolymer, copolymer or mixture of said polymers having recurring units of the formula: ##STR4## alone or together with recurring units of the formula: ##STR5## wherein each SO.sub.2 group can be in the ortho, meta or para position, b represents the integer of 1 or 2 and R represents ##STR6## wherein each R' independently represents a C.sub.1 -C.sub.3 alkyl, and n is an integer of 0 or 1.

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L3: Entry 17 of 30 File: USPT

DOCUMENT-IDENTIFIER: US 5762798 A
TITLE: Hollow fiber membranes and method of manufacture

Abstract Text (1):
An asymmetrical, microporous, hollow fiber membrane is made from a polymeric dope mixture of polysulfone and polyvinyl pyrrolidone dissolved in an aprotic solvent. The physical morphology of the hollow fiber membrane, i.e., the asymmetric microporous wall, is rapidly formed by passing the polymeric dope mixture through an outer annular orifice of a tube-in-orifice spinneret while simultaneously passing a precipitating solution through the central tube of the spinneret. The emerging hollow fiber travels substantially downward for about 0.01-10 m before submersion into a quenching bath. The asymmetrical, microporous, hollow fiber membrane is biocompatible and suitable for use in, for example, dialysis, hemodialysis, ultrafiltration, and water filtration applications.

Brief Summary Text (3):
The invention relates to improved hollow fiber membranes and an improved process for the production of those membranes. In particular, the invention relates to improved asymmetrical microporous hollow fibers incorporating a polysulfone, a polysulfone with a low molecular weight surfactant or a polyimide. The asymmetrical, microporous hollow fibers incorporating a low weight surfactant have improved flux and rewetting characteristics. The asymmetrical, microporous hollow fibers incorporating a polyimide have low water or blood leachable impurities.

Brief Summary Text (4):
The unique process for the production of these membranes involves passing a polymeric solution through an outer annulus of die to create an annular stream and a precipitating fluid through the inner orifice of the die creating a stream within the annular stream resulting in hollow fiber formation.

Brief Summary Text (6):
A microporous, hollow fiber is a polymeric capillary tube having an outside diameter of less than or equal to 1 mm, and whose wall functions as a semipermeable membrane. The fibers are useful in separation processes involving transport mainly through sorption and diffusion. Such processes include dialysis, hemodialysis, ultrafiltration, hemofiltration, plasma filtration, blood separation drug release in artificial organs and water filtration where ultra-pure water is needed such as in the electronic and pharmaceutical industries. Each of these applications have various requirements including pore size, strength, biocompatibility, cost and speed of production and reproducibility.

Brief Summary Text (7):
Given the varying uses to which this fiber may be applied, it is highly desirable that the hollow fiber membrane have as little leachable impurities as possible in water, blood, from 0% to saturated solutions of NaCl in water, and other similar type of aqueous solutions. For certain applications, it may also be desired that the membranes be easily or immediately wettable by water, blood and other types of aqueous solutions without the need for costly polymer additives, post fiber-formation treatments with wetting agents or both. In other applications, it would be highly desirable for these membranes to remove endotoxin from the solution to be filtered. In still other applications, it may be desirable to be able to repeatedly autoclaved without the loss of the rewetting characteristic.

Brief Summary Text (8):
Early hollow fibers have included regenerated cellulose material and modified

polyacrylonitrile material. However, it is difficult to control the porosity and pore size of these fibers, and for some applications, composite membranes consisting of an ultra-thin layer contiguous with a more porous substrate are needed to provide the necessary strength.

Brief Summary Text (9):
Early hollow fiber membranes have also been prepared from hydrophobic polymers such as polysulfones, aromatic polyamides and polyimides, and polyamide-imides. However, the hydrophobic nature of these polymer presents difficulties with wetting these membranes when used in aqueous systems. Therefore, hydrophilic polymers such as polyvinyl alcohol, polyvinyl acetate co-polymers, polyvinylpyrrolidone and polyvinylpyrrolidine have typically been incorporated directly into the fibers to achieve a hydrophilic fiber that wets easily. Alternatively, polyethylene glycol, glycerol and/or a variety of surfactants have been incorporated directly into the fibers or used post-fiber formation to achieve wettability.

Brief Summary Text (11):
The polymer solution generally comprises about 15-65 combined weight-% of a first, fiber forming polymer and a second polymer. Fiber forming polymers disclosed include polysulfone and polyaromatic polyamide polymers. Polymers disclosed for use as the second polymer are polyvinylpyrrolidone polymers. The solvent for the polymer solution disclosed in the examples of the patent is dimethylacetamide (DMA) and dimethylformamide (DMF). Precipitating liquid disclosed in Klein include water/DMA, air and water/isopropyl alcohol. The fibers prepared by the process of Klein are designed only to be used as the support structure of a final composite membrane. The actual selective membrane is applied as an ultrathin coating to this support structure in an additional step or steps. Further, this process is a relatively slow, time consuming step wherein fiber is produced at a rate of about 20 m/min.

Brief Summary Text (13):
This limitation is borne out in another patent drawn to a method for making fibers for hemodialysis, Heilmann, U.S. Pat. No. 4,906,375. This patent discloses a process comprising wet spinning a polymer solution made up of a solvent, about 12 to 20 wt. % of a first, hydrophobic polymer and 2-10 wt. % of a hydrophilic polyvinylpyrrolidone polymer and simultaneously passing through a hollow internal core a precipitant solution comprising an aprotic solvent in conjunction with at least 25 wt. % non-solvent. Hydrophobic polymers disclosed include polysulfones such as a polyether sulfone, polycarbonates, and polyamides. The polar aprotic solvents disclosed include dimethylformamide (DMF), dimethylsulfoxide (DMSO), dimethylacetamide (DMA), n-methylpyrrolidone and mixtures thereof. The precipitating liquor is in the form of the aprotic solvent in conjunction with a certain amount of non-solvent, usually water. While this patent does not disclose a rate of production of the hollow fiber, we have found that, in accordance with the predictions of Joh et al., the Heilmann process can only be run at about 15-20 meters per minute. Further, the hollow fiber membranes produced by this process have limitations in hydrophilicity, water flux, etc. and by their very nature are limited in use to dialysis applications.

Brief Summary Text (14):
U.S. Pat. No. 4,432,875 to Wrasidlo et al., discloses reverse osmosis fiber membranes made from specific polyimide structures. Baked onto the membrane is a polymeric, high molecular weight surfactant. The polymeric surfactant apparently takes the place of the hydrophilic polymer Heilmann reference and is used to increase the wettability of the resultant fiber membrane. The fiber produced using the Wrasidlo process, however, is limited to sheet membranes that have a porosity significantly different than microporous hollow fiber membranes. Further, the "baking on" of the surfactant in Wrasidlo results in a fiber that is costly to manufacture, thus making the fiber's use economically impractical for smaller companies.

Brief Summary Text (15):
U.S. Pat. No. 3,719,640 to Le et al., discloses linear polymers of polyamide-imides having a specific formulation containing a quaternizable nitrogen atom. When nitrogen is quaternized, the polymer becomes hygroscopic and may be used as separatory membranes in such processes as desalination.

Brief Summary Text (16):
U.S. Pat. No. 4,900,449 to Kraus et al., discloses the use of polyimide polymers for pleated flat sheet type membranes. The membranes and process described are limited in use to flat sheet membranes for water filtration applications. Such membranes have less than one-half the surface area available for filtration as the filter membranes of the

present invention.

Brief Summary Text (17):
Many hollow fiber membranes utilize glycerol to impart the rewetting and flux characteristics of the fiber. However, the addition of glycerol to the fiber makes the fiber costly to manufacture. Further, the glycerol must be thoroughly rinsed prior to use or it will contaminate the piping system. This makes glycerol-coated fibers inefficient, costly and time consuming for the end user. In addition, if the glycerol were not used in the fiber, the fiber would have a much lower flux rate.

Brief Summary Text (18):
While the fibers discussed above are useful in many applications, there is and always has been a trade-off among properties including tensile strength, elasticity, porosity, flux, and sieving characteristics including molecular size cutoff, solute clearance, etc. Thus, new membranes are constantly needed that can offer advantages in particular applications with given property requirements. The fiber membranes discussed above each have their own particular advantages and disadvantages, e.g., Klein teaches a fiber which can withstand high pressures present in reverse osmosis systems, Heilmann discloses a fiber which is tailored to dialysis systems, having lower flux and more stringent sieving properties, and Wrasidlo discloses membranes for reverse osmosis and filtration processes. However, not one of these references teach an asymmetric, microporous hollow fiber membrane which is biocompatible and equally suitable in processes such as hemofiltration, plasma filtration, hemodialysis and water purification and which does not use some type of polymer "additive" to render the resultant membrane hydrophilic or uses a surfactant to accomplish that goal that does not need to be "baked on."

Brief Summary Text (19):
A hollow fiber membrane that could be applied across a wide range of applications would provide a decided advantage over early hollow fiber membranes. A new and useful hollow fiber membrane is needed that incorporates a low molecular weight. surfactant which does not require the use of high temperatures to ensure the incorporation of the surfactant into and/or onto the membrane resulting in a membrane that can be autoclaved repeatedly without the loss of the rewetting characteristic and one which does not rely on glycerol for rewettability.

Brief Summary Text (20):
In addition, a new and useful membrane is needed that is chemically inert to blood and water solutions, or both, within the normal blood pH range of 7.35-7.45 and also be rewettable after repeated sterilizations. In cases where the membrane will be used for medical applications or applications involving the semi-conductor industry it would also be desirable that leachable additives such as surfactants and/or hydrophilic polymers are completely absent from the resultant fiber because residual toxic substances are a major concern. In cases where the membrane will be in contact with human blood, it is also highly desirable that the membrane be biocompatible in that it will not activate complement and that it have high sieving coefficients for middle molecules (5,000 daltons to 25,000 daltons molecular weight) such as .beta..sub.2 microglobulin and myoglobin.

Brief Summary Text (21):
Further, the relatively slow rate at which related art hollow fibers are produced results in costly to manufacture microporous hollow fibers. Therefore, a new and useful process is also needed to produce the membranes of the present invention to reduce significantly the manufacture time thus ensuring that a low cost hollow fiber is available to large and small companies alike.

Brief Summary Text (23):
It is an object of the improved hollow fiber membranes provided in accordance with the present invention and the process for preparing the same to solve the problems outlined above that have heretofore inhibited the successful production of a cost-efficient membrane that has a broad range of applications.

Brief Summary Text (24):
It is also an object of the present invention to achieve a quantum jump in production rates by utilizing a sophisticated combination of process steps for the production of all hollow fiber membranes disclosed herein. A first embodiment of the present invention provides improved processing conditions that result in uniform creation of a liquid annular solution of polymer surrounding the precipitating liquid core that rapidly and uniformly solidifies into a microporous hollow fiber. Production rates can

be significantly increased without failure of the hollow fiber membrane.

Brief Summary Text (26):
A second embodiment of the present invention utilizes a microporous hollow fiber membrane incorporating a surfactant that enables the use of a unique hollow fiber that, as will be shown, has greatly improved flux and rewetting characteristics than conventional art fibers.

Brief Summary Text (27):
The hollow fiber with surfactant includes about 75 to 99 dry wt. % of a hydrophobic polysulfone polymer, about 0.1 to 20 dry wt. % of a hydrophilic polyvinylpyrrolidone polymer and an effective amount of a low molecular weight surfactant sufficient to enable the membrane to exhibit a flux of at least about 5.times.10.sup.-5 mL/min/cm.sup.2 /mmHg wherein the membrane is capable of maintaining significant flux characteristics for up to at least five use and drying cycles. In addition, as will be shown, the fiber has superior rewetting characteristics, "rewetting" being defined as the ability of the fiber's flux to continuously return after at least five drying and wetting cycles.

Brief Summary Text (28):
The process for producing this unique membrane includes the steps of (a) forming an annular liquid by passing a polymeric solution comprising about 5 to 25 wt. % of a hydrophobic polysulfone polymer and about 1 to 25 wt. % of a hydrophilic polyvinyl-pyrrolidone polymer dissolved in an aprotic solvent and having a viscosity of about 100 to 10,000 cps through an outer annular orifice of a tube-in-orifice spinneret, (b) passing a precipitating solution comprising about 0.1 to 100 wt. % of an organic solvent and about 0.1 to 100 wt. % of water into the center of the annular liquid through the inner tube of the spinneret, (c) passing the polymer precipitate through the atmosphere or an augmented atmosphere, (d) quenching the polymer precipitate in a bath to form a hollow fiber, (e) contacting the polymer precipitate with a solution comprising about 0.01 to 10 wt. % of a low molecular weight surfactant, and (f) taking up the fiber at a rate of about 125-250 ft/min.

Brief Summary Text (30):
One of the advantages of the hollow fiber membrane incorporating a surfactant is that hollow fibers treated with surfactant retain, as will be shown, their "rewetting" character after repeated washing and autoclaving without the use of glycerol. Another advantage of the hollow fiber membrane incorporating a surfactant is that the surfactant may be incorporated on and/or into the hollow fiber without the need to covalently bond the fiber as in heat bonded surfactant to fiber. More significantly, this provides a ready-to-use, rewettable hollow fiber membrane without the use of glycerol.

Brief Summary Text (31):
A third embodiment of the present invention provides a hollow fiber membrane incorporating a polyimide. It is an object of the hollow fiber membrane incorporating a polyimide and process for preparing the same to provide a unique hollow fiber membrane that, as will be shown, is chemically inert to aqueous solutions and/or blood, is rewettable after repeated steam and/or chemical sterilizations of at least 6-7 times, has superior clearance, sieving, and water permeability characteristics.

Brief Summary Text (32):
The hollow fiber membrane incorporating a polyimide includes about 15-25 wt. % of a fiber forming polymer selected from the group of polyimides and is characterized by the absence of polymer additives which increase wettability, wherein the hollow fiber membrane has a pore size range such that it rejects 100% of molecules (sieving coefficient of 0.0) having a molecular weight greater than about 65,000 daltons, and rejects 0.0% of molecules (sieving coefficient of 1.0) having a molecular weight of about 6,000 daltons and less, and rejects from about 35% to 0.0% of molecules (sieving coefficient of 0.65 to 1.0) having a molecular weight of 17,000 daltons; and wherein at a blood flow rate of 300 mL/min and 1.35 m.sup.2 of active surface area, the fiber has clearance rates of 225-270 for urea, 200-250 for creatinine, 170-225 for phosphate, and 125-150 for Vitamin B.sub.12 and wherein the fiber has high sieving coefficients of 0.0 for albumin, 0.65-1.0 for myoglobin, and 1.0 for inulin.

Brief Summary Text (33):
The method of manufacturing the hollow fiber membranes incorporating a polyimide includes the steps of (a) dissolving the undegraded polyimide in the appropriate solvent system (b) forming an annular liquid by passing the polymeric solution

comprising about 15-25 wt. % of a highly polar polyimide dissolved in an organic solvent and having a viscosity of about 1500-5000 cps through an outer annular orifice of a tube-in-orifice spinneret, (c) passing a precipitating solution comprising about 65-99 wt. % of an organic solvent and about 35-1 wt. % of water into the center of the annular liquid through the inner tube of the spinneret, (d) passing the polymer precipitate through the atmosphere or an augmented atmosphere, (e) quenching the polymer precipitate in a bath to form a hollow fiber; and (f) taking up the fiber at a rate of about 40-70 m/min.

Brief Summary Text (34):
The most significant advantage of the hollow fiber membranes incorporating a polyimide is that membranes so formed immediately wets with aqueous solutions without the use of PVP, glycerine, or other additives. This results in an economical fiber with a homogeneous sponge structure that requires no further mechanical, chemical or other treatment to establish aqueous solution wettability.

Drawing Description Text (5):
FIG. 4A is an enlarged, microscopic, cross-sectional view of the hollow fiber membrane incorporating a polyimide in accordance with the present invention illustrating the "homogeneous sponge-like" structure;

Drawing Description Text (7):
FIG. 5 is an enlarged detailed view of the hollow fiber membrane incorporating a polyimide in accordance with the present invention illustrating the homogenous sponge-like structure taken at a 45.degree. angle of cross-section;

Drawing Description Text (8):
FIG. 6A is an enlarged, microscopic cross-sectional view of prior art hollow fiber membranes illustrating "voids";

Drawing Description Text (10):
FIG. 7 is an enlarged, microscopic cross-sectional view of hollow fiber membranes with voids.

Detailed Description Text (7):
The pore size of the membrane and the molecular weight cutoff will vary depending on the application, i.e. water filtration, ultrafiltration, hemofiltration, plasma filtration (plasmapheresis) etc. However, we define microporous generally to mean membranes having a pore size ranging substantially from about 0.001 .mu.m to 0.5 .mu.m. We also define "flux" or "water permeability" to mean a measure of the volume of water passed by the hollow fiber membrane under pressure for a given time and area. "Rewetting" and similar words such as rewettable, rewettability, etc., as used herein, is a description of the ability of a membrane to maintain a particular level of flux or water permeability after either cycles of wetting and drying the membrane or after steam or chemical sterilization. "Asymmetric" means that the pore size of the fiber varies from smaller to larger from the inner barrier layer to the outer sponge-like layer, respectively. "Uniformly porous" and "sponge-like" means that the porosity of the hollow fiber membrane is homogeneous throughout. In addition, "solvents with respect to the polymer" are typically aprotic solvents while "non-solvents with respect to the polymer" are typically protic solvents. "Anti-solvent" is a nonsolvent with respect to the polymer and is used herein when referring to additional nonsolvents that are added to the polymeric solution. "Nonsolvents," on the other hand, are also nonsolvents with respect to the polymer, but is used herein when referring to nonsolvents added to the precipitating solution.

Detailed Description Text (8):
A. Improved Fiber Spinning Process for the Preparation of Asymmetric, Microporous, Hollow Fiber Membranes. The first embodiment of the invention is directed to a spinning process for forming microporous, hollow fibers from a polymeric solution comprising a fiber-forming polysulfone polymer, a polyvinyl pyrrolidone polymer and an aprotic solvent. The fiber forming polysulfone polymer is preferably a polyarylene sulfone. More preferably, the polysulfone polymer is a polysulfone polymer having the formula: ##STR1## available from Amoco Chemicals Corp. under the UDEL mark, a polyether sulfone having the formula: ##STR2## available from ICI America, Inc. under the VICTREX mark, a polyaryl sulfone, available from Amoco Chemicals Corp. under the RADEL mark, or a mixture thereof. Most preferably, the polysulfone polymer is a polysulfone of formula (I).

Detailed Description Text (15):

The polymeric solution is spun from the outer, annular orifice of a tube-in-orifice spinneret. A precipitating solution is delivered to the tube of the spinneret. The precipitating solution comprises a lower alcohol and water and may further comprise an aprotic solvent. To some extent, the composition of the precipitating solution affects the porosity, clearance and flux properties of the fiber. The composition of the precipitating solution effective to produce a hollow fiber membrane for use in hemodialysis is illustrated below in Table I.

Detailed Description Text (16):
In another preferred embodiment, a precipitating solution effective to produce a hollow fiber membrane for use in a hemofilter operation may comprise the components illustrated in Table II.

Detailed Description Text (17):
In yet another preferred embodiment, a precipitating solution effective to produce a hollow fiber membrane for use in a blood filter to separate red blood cells from higher molecular weight materials may comprise the components illustrated in Table III.

Detailed Description Text (21):
The proportions of the alcohol, water and aprotic solvent which make up the precipitating solution influence the morphology, clearance, permeability, selectivity etc. of the hollow fiber membrane. In particular, the absence of an aprotic solvent in the precipitating solution may result in lower poor size and lower flux in the resulting fiber. It is generally preferred that the proportion of water in the precipitating solution remain relatively low, about 10 to 35 wt. %, to ensure proper fiber results less than about 10 wt. % of water may result in too slow of a precipitation of the polymers to form a fiber, and a concentration of water greater than about 35 wt. % may result in a decrease in flux and pore size.

Detailed Description Text (31):
The hollow fibers may then be dried, texturized, cut to a desired length, or further processed to form useful articles including hemodialyzer, hemofilters, blood filters, water filters, etc, having performance levels at least equivalent to currently available hollow fiber membranes.

Detailed Description Text (36):
A polymeric dope solution was formed by dissolving 16.2 wt. % of a polysulfone polymer having a molecular weight of about 55,000 to 60,000 (UDEL P1800 available from Amoco) and 4.8 wt. % polyvinyl pyrrolidone polymer (PVP) having a K-value of about 85-88 in dimethylacetamide (DMA). The material was filtered and then pumped to a tube-in-orifice spinneret at a rate of 3.1 mL/min and a temperature of about 35.degree. C.

Detailed Description Text (56):
The procedure of Example 1 was repeated using a dope solution comprising about 15.1 wt. % of a polysulfone polymer having a molecular weight of about 60,000 to 65,000 (UDEL P1835 from Amoco) and about 2.8 wt. % of PVP having a K-value of about 85-88 in DMA and a diluent solution comprising about 80 wt. % isopropyl alcohol and about 20 wt. % r.o.,d.i. water. The resulting dope solution had a viscosity of about 1520 cP at 25.degree. C. The dope solution was supplied to the spinneret at about 37.degree. C. and a rate of about 3.55 mL/min, and the diluent solution was supplied at a rate of about 2.5 mL/min. The spinneret head was maintained at about 26.degree. C. The fiber was spun into the ambient atmosphere.

Detailed Description Text (64):
The procedure of Example 1 is repeated using a dope solution comprising about 15.1 wt. % of UDEL 1835 and 2.8 wt. % PVP having a K-value of about 85-88 in DMA and a diluent solution comprising about 79 wt. % isopropyl alcohol and about 21 wt. % r.o.,d.i. water. The dope solution is supplied to the spinneret at about 37.degree. C. and a rate of about 3.55 mL/min, and the diluent solution is supplied at a rate of about 2.5 mL/min at about 20.degree. C. The fiber is spun into the ambient atmosphere.

Detailed Description Text (75):
The procedure of Example 1 was repeated using a dope solution comprising about 15.1 wt. % of a polysulfone polymer having a molecular weight of about 60,000 to 65,000 (UDEL P1835 from Amoco) and about 2.8 wt. % of PVP having a K-value of about 85-88 in DMA and a diluent solution comprising about 81 wt. % isopropyl alcohol and about 19 wt. % r.o.,d.i. water. The dope solution was supplied to the spinneret at about 34.degree. C. and a rate of about 3.55 mL/min, and the diluent solution was supplied at a rate of about 2.5 mL/min. The spinneret head was maintained at about 19.degree. C. The fiber

was spun into the ambient atmosphere.

Detailed Description Text (79):
The procedure of Example 1 was repeated using a dope solution comprising about 15.1 wt. % of a polysulfone polymer having a molecular weight of about 60,000 to 65,000 (UDEL P1835 from Amoco) and about 2.8 wt. % of PVP having a K-value of about 85-88 in DMA and a diluent solution comprising about 82 wt. % isopropyl alcohol and about 18 wt. % r.o.,d.i. water. The dope solution was supplied to the spinneret at about 34.degree. C. and a rate of about 3.55 mL/min, and the diluent solution was supplied at a rate of about 2.5 mL/min. The spinneret head was maintained at about 20.degree. C. The fiber was spun into the ambient atmosphere.

Detailed Description Text (91):
B. Asymmetric, Microporous, Hollow Fiber Membrane Incorporating a Surfactant. The second embodiment of the present invention is directed to a microporous, hollow fiber that includes a hydrophobic polymer, a hydrophilic polymer and a low molecular weight surfactant. When used as a water filter, the pore size of the microporous, hollow fiber membrane incorporating a surfactant is typically from about 0.005 .mu.m to 0.5 .mu.m with the average pore size being from about 0.05 .mu.m to about 0.1 .mu.m.

Detailed Description Text (92):
The hydrophobic polymer is preferably a polysulfone polymer, polyethersulfone, poly(arylsulfone), poly(aryl ether sulfone) or a poly(phenylsulfone). The polysulfone polymer is preferably a poly(arylsulfone). More preferably, the polysulfone polymer is a poly(oxy-1,4-phenylene sulfonyl-1,4-phenyleneoxy-1,4phenyleneisopropylidene-1,4phenylene) polymer having the formula (--OC.sub.6 H.sub.4 C(CH.sub.3).sub.2 C.sub.6 H.sub.4 SO.sub.2 C.sub.6 H.sub.4 --).sub.n with the accompanying structure: ##STR4## available from Amoco Chemicals Corp. (Atlanta, Ga.)) under the UDEL mark; or

Detailed Description Text (93):
a polyether sulfone having the formula (--O--C.sub.6 H.sub.4 SO.sub.2 C.sub.6 H.sub.4 --) with the accompanying structure: ##STR5## available from ICI Americas, Inc. (Wilmington, Del.) under the VICTREX mark; or a poly(arylsulfone) available from Amoco Chemicals Corp. (Atlanta, Ga.) under the RADEL mark, or a mixture thereof. Most preferably, the polysulfone polymer is a polysulfone of formula (I).

Detailed Description Text (95):
The hydrophilic polymer not only supplies hydrophilicity to the hollow fiber membrane but also markedly improves its porosity as well. The hydrophilic polymer may be water soluble cellulose, starch derivatives, polyvinylpyrrolidone, polyethylene glycols. Preferably, the hydrophilic polymer is polyvinylpyrrolidone ("PVP").

Detailed Description Text (102):
It should be noted that the actual concentration of surfactant in the soaking solution is dictated by processing restraints. At higher concentrations, flush time needed to remove excess surfactant from the fiber is increased. At lower concentrations, longer soaking times are required to obtain effective membranes.

Detailed Description Text (104):
The hollow fiber membranes in accordance with the present invention have improved flux characteristics as discussed previously. The fiber surface may well be modified with surfactant so as to reduce inter and/or intra molecular surface tension and/or water wettability. This may enable the opening of previously closed pore structure helping to account for increased water flux across the membrane. When the treated fibers were examined under high magnification scanning electron microscopy (SEM), no apparent change in fiber structure was noted. Further, it also appears that the effective molecular size cutoff is numerically increased using the membranes of the present invention. For example, using bovine serum albumin (BSA) as a molecular marker (0.5 g/L), a BSA (in reverse osmosis water) rejection test showed a significant increase in the effective pore size for the surfactant treated fiber. A non-treated fiber, on the other hand, showed approximately 99% BSA rejection as opposed to treated fibers which showed a 70% rejection of BSA. The surfactant does not wash out of the fiber completely, even with repeated use and drying cycles.

Detailed Description Text (109):
The polymeric solution is spun from the outer, annular orifice of a tube-in-orifice spinneret. A precipitating solution is delivered to the tube of the spinneret. The precipitating solution preferably includes a protic solvent, an aprotic solvent and

water and combinations thereof. To some extent, the composition of the precipitating solution affects the porosity, clearance, tensile strength, wall thickness, inner and outer diameters and flux properties of the fiber. The practitioner of ordinary skill in the art will recognize that the precipitating solution compositions outlined in the following tables are helpful to direct the practitioner in selecting a useful formulation for a desired fiber end use. The selection of particular components and proportions is obviously up to the practitioner. The composition of the precipitating solution effective to produce a hollow fiber membrane for use in hemodialysis is illustrated below in Table IX.

Detailed Description Text (110):
Precipitating solutions effective to produce a hollow fiber membrane for use in a hemofilter operation may comprise the components in proportions as illustrated in Table X.

Detailed Description Text (111):
Precipitating solutions effective to produce a hollow fiber membrane for use in a-blood filter to separate red blood cells from higher molecular weight materials may comprise the components in proportions as illustrated in Table XI.

Detailed Description Text (112):
Precipitating solutions effective to produce a hollow fiber membrane for use in water filtration may comprise the components in proportions as illustrated in Table XII.

Detailed Description Text (117):
The proportions of the alcohol, water and aprotic, solvent which make up the precipitating solution influence the morphology, clearance, permeability, selectivity, etc. of the hollow fiber membrane. It is generally preferred that the proportion of water in the precipitating solution remain relatively low, about 2 to 35 wt. %, to ensure that a fiber having desirable characteristics is produced. If the precipitating liquid contains less than about 2 wt. % water, the resultant: precipitation of the polymers may be too slow to form a fiber. On the other hand, a precipitating liquid that has a concentration of water greater than about 35 wt. % may result in a fiber having decrease flux with a small pore size.

Detailed Description Text (127):
The surfactant may be incorporated into or onto the hollow fiber membrane through a number of mechanisms. The polymeric spinning solution itself may comprise about 0.01 to 10 wt. % of surfactant. In other useful embodiments, about 0.01 to 10 wt. % of a surfactant may be incorporated into the quenching bath, rinse bath, take-up reel bath, a surfactant bath or any other process step wherein the gelled tube or precipitated hollow fiber is contacted with an aqueous or organic solution, or both. In a preferred embodiment, the fiber is cut and formed into bundles that are then soaked in a surfactant solution.

Detailed Description Text (128):
Preferably, the hollow fiber membrane or gelled polymeric solution has a contact time with a surfactant solution of less than about 10 seconds. If the surfactant is incorporated into the quenching bath, rinse bath or take-up reel bath, the fiber's residence time in the solution is about 4 to 48 hours. In another embodiment, the fibers are cut and bundled prior to soaking in the surfactant solution for less than 72 hours, more preferably for less than 30 hours and most preferably for less than 24 hours.

Detailed Description Text (132):
Water flux is determined by a test developed in-house. Specifically, the water flux is measured on test mat size (0.02 to 0.08 m.sup.2) bundles which are potted in a polycarbonate cylindrical case. A transmembrane pressure of 5 psi is maintained across the unit as reverse osmosis water is pumped through one of two side ports (one side port clamped off), exiting out one of two end ports (one end port clamped off). The water is collected via graduated cylinder on a timed basis to determine flux. Drying of the membrane may be accomplished by circulating dry air through and around the hollow fiber membranes. The flux of a fiber which has been cycled in this manner can be compared to its original values to determine the membrane's rewettability. The process is repeated in duplicate to insure reproducibility.

Detailed Description Text (156):
The membranes made from the examples above were measured for flux, rewettability and diffusional flow rates. The water flux was measured on test mat size (0.02 to 0.08

m.sup.2) bundles which were potted in a polycarbonate cylindrical case. A transmembrane pressure of 5 psi was maintained across the unit as reverse osmosis water was pumped through one of two side ports (one side port clamped off), exiting out one of two end ports (one end port clamped off). The water was collected via graduated cylinder on a timed basis to determine flux. Drying of the membrane was accomplished by circulating dry air through and around the hollow fiber membranes. The flux of fibers cycled in this manner were compared to their original values to determine the membrane's flux and rewettability characteristics.

Detailed Description Text (157):
The hollow fiber membranes were also tested for diffusional air flow, a method of determining the integrity of a membrane. When dry, air flow easily through the pores in the membrane; when wet, air does not flow through an intact membrane. Membranes were wet with reverse osmosis water to fill the pores. A transmembrane pressure equal to 30 psi was applied to the upstream side of the membrane. Air which diffuses through is measured to determine the integrity of the membrane.

Detailed Description Text (159):
A filter module comprising approximately 1.4 m.sup.2 of membrane prepared in accordance with Example 17 was tested in accordance with the previously disclosed flux test. The module produced a water flux of 0.0026 mL/min/mmHg/cm.sup.2. The module also produced a diffusional air flow of 20 mL/min at 30 psi inlet air pressure.

Detailed Description Text (161):
A filter module comprising approximately 1.4 m.sup.2 of membrane fabricated in accordance with Example 18 was tested for its ability to rewet upon successive dryings. Each wet dry cycle trial consisted of the following steps:

Detailed Description Text (167):
A filter module comprising approximately 1.4 m.sup.2 of membrane fabricated in accordance with Example 19 was tested for its rewetting characteristics and its ability to remove bovine serum albumin from blood. Each rewetting test trial consisted of the following steps:

Detailed Description Text (174):
A filter module comprising approximately 3.0 m.sup.2 of membrane fabricated in accordance with Example 20 was tested for its initial flux rate and diffusional flow characteristics. The module produced a water flux of 0.00146 and a diffusional air flow of 53 mL/min.

Detailed Description Text (176):
A filter module comprising approximately 3.0 m.sup.2 of membrane fabricated in accordance with Example 21 was tested for its initial flux rate and diffusional flow characteristics. The module produced a water flux of 0.00092 and a diffusional air flow of 51 mL/min.

Detailed Description Text (177):
C. Asymmetric, Microporous, Hollow Fiber Membrane Incorporating a Polyimide. The third embodiment of the present invention is directed to an asymmetrical microporous, hollow fiber membrane that includes a polyimide polymer that is highly polar. The membrane is particularly well suited for medical applications where the membrane will come into contact with blood because it is biocompatible, does not activate complement, and has the remarkable ability to exhibit high sieving coefficients for middle molecules such as .beta..sub.2 microglobulins and myoglobins. When used as a membrane for dialysis applications, the membrane has a pore size ranging from substantially about 0.001 .mu.m to substantially about 0.01.mu.m with the average pore size being from substantially about 0.003 .mu.m to substantially about 0.005 .mu.m.

Detailed Description Text (178):
Also surprisingly, the membrane is equally suited in all filtration applications for its unique ability to completely remove existing endotoxin from the solution being filtered.

Detailed Description Text (179):
When this unique membrane is used as a water filter, the pore size preferably ranges from about 0.005 .mu.m to about 0.5 .mu.m with an average pore size of from about 0.05 .mu.m to about 0.1 .mu.m. When used as a plasma filtration membrane the maximum pore size ranges from substantially about 0.1 .mu.m to substantially about 0.2 .mu.m

Detailed Description Text (180):
The highly polar polymer in accordance with the present invention is preferably an aromatic polyimide that when precipitated as a membrane is immediately wettable without the use of polymer additives or surfactants. The preferred polyimide in accordance with the present invention is disclosed in U.S. Pat. No. 3,708,458 to Alberino which is hereby incorporated by reference. The polyimide is prepared from benzophenone-3,3',4,4'-tetracarboxylic acid dianhydride and a mixture of 4,4'-methylenebis(phenyl isocyanate) and toluene diisocyanate (2,4- or 2,6-isomer) of-mixtures thereof. The polyimide includes the recurring group: ##STR7## wherein 10% to 90% of the R groups are ##STR8## and the remaining R groups include either ##STR9##

Detailed Description Text (185):
As stated previously, no additional additives, such as polyvinylpyrrolidone, polyethylene glycol, glycerine, cellulose or starch derivatives or amphoteric, zwitterionic, nonionic, anionic, or cationic surfactants, are needed to produce a hollow fiber membrane that wets immediately upon contact with blood, water and other aqueous solutions and maintains the rewettability for at least 6-7 sterilizations by steam or chemicals. Because no additional polymers are needed to make the resultant fiber wettable, the choice of solvents for use as the precipitating solution is critical in influencing the hydrophilicity, structure and porosity of the fiber. In addition, the elimination of additives in the polymeric dope solution decreases and virtually eliminates all but trace amounts of solids and/or oxidizable material that is leachable from the resultant fiber. Further, the structural integrity of the resultant hollow fiber membrane is more stable after the removal of the solvent and/or antisolvents and nonsolvents.

Detailed Description Text (186):
Initially, the polyimide polymer is dissolved in a solvent. Preferably, this solvent is also miscible with water. A representative, non-limiting list of solvents useful in the invention includes dimethylformamide (DMF), dimethylsulfoxide (DMSO), dimethylacetamide (DMA), n-methylpyrrolidone, and mixtures thereof. Preferably, the solvent is DMF, an aprotic solvent. Depending on the desired properties of the hollow fiber, a small amount of an antisolvent may be added in small quantities to the primary solvent that is used. The addition of an antisolvent in the polymer forming solution will enhance the desired precipitate characteristics of the polymer during fiber formation. For example, adding acetic acid in the amount of 4-7 wt. % ensures that the fiber has a uniform sponge-like structure, free of voids, large vacuous spaces extending from the inner membrane wall to the outer membrane wall that can permit the passage of large molecular weight molecules if the void pierces the inner and/or outer membrane wall. Alternatively, additional amounts of solids may be added to the polymer solution up to 25.0 wt. % to solve this problem. The homogeneous, sponge-like structure may also be achieved in accordance with the process and formulations described herein.

Detailed Description Text (187):
FIG. 4A depicts a cross section of a hollow fiber membrane in accordance with the present invention magnified 130.times. taken on a Hitachi S-800 scanning electron microscope. FIG. 4B which is a 10.times. magnification (1300.times.) of the area enclosed by box 4B in FIG. 4A and illustrates the "uniform sponge-like structure" 200 of hollow fiber membranes in accordance with the present invention. FIG. 5 is a 10,000.times. view taken at a 45.degree. angle of cross-section of hollow fibers in accordance with the present invention showing the outer membrane wall 210 and the sponge-like inner composition 215. "Voids" 220, which characterize many hollow fiber membranes, may be seen by referring to FIGS. 6A (130.times.) and 6B (1300.times.). The absence of voids in the formed hollow fiber membrane results in a mechanically stronger fiber with enhanced diffusion rates.

Detailed Description Text (189):
Higher polyimide solids may be employed in organic solvent systems if spinneret housings, feed lines, and polymer solution tanks are heated. Upon heating, the viscosity of the polymer solution is lowered, allowing otherwise unusable polymer solution formulations to be spun. Depending upon the composition of the precipitating solution the skilled practitioner chooses, heating and/or cooling the system may influence the morphology and performance characteristics of the resultant fiber membrane.

Detailed Description Text (192):
For example, as the weight percent of the solvent with respect to the polymer increases, fiber formation is impaired and is characterized by a "glassy"0 weaker structure and it becomes increasingly difficult to "pull" the fiber. Conversely, as the

weight percent of the solvent with respect to the polymer decreases and the weight percent of water and/or other non-solvents with respect to the polymer increases, voids are seen in the fiber structure which may allow high molecular weight molecules to pass through the fiber if they pierce the outer membrane wall. This may best be seen in FIG. 7 which illustrates a fiber cross-section magnified 130.times. with voids 221 that resulted from using a precipitating solution with an increased weight percent of non-solvent with respect to the polymer. In addition, as the weight percent of water and/or other non-solvents with respect to the polymer increases, a low pore density on the outer fiber wall and a tighter closed inner wall with a low flux is seen. It will therefore be appreciates by those skilled in the art that the selection of the composition of the precipitating solution is crucial.

Detailed Description Text (193):
The composition of the precipitating solution effective to produce a hollow fiber membrane for use in hemodialysis, as well as, water filters, autologous blood filters, and plasma filters is illustrated below in Table XIII.

Detailed Description Text (198):
The proportions of the water, and other non-solvents (e.g. alcohol) which may make up the precipitating solution influence the morphology, clearance, permeability, and selectivity characteristics of the hollow fiber membrane. In particular, the total absence of a solvent with respect to the polymer in the precipitating solution may result in a small number of pores in the fiber wall as well as lower flux. Further, water is clearly an important ingredient in the precipitating solution used in this membrane formation process.

Detailed Description Text (199):
Because the addition of water affects the performance characteristics of the resultant fiber membrane it is generally preferred that the proportion of water in the precipitating solution be about 1-35 wt. %, to ensure proper fiber performance characteristics. Less than about 10 wt. % of water may result in the polymeric solution precipitating too slowly forming a fiber with increased pore size. This is desirable to form a fiber for use in water filters but would not, for example, form a fiber suitable for use as a dialyzer fiber. Conversely, a concentration of water greater than about 35 wt. % results in a fiber with lower pore density on the outside and a tighter closed inner wall with a general decrease in flux. However, when the proportion of water falls within 1-35 wt. %, we see enhanced uniformity in the desirable sponge-like structure and the hollow fiber membrane is characterized by the complete absence of voids. This uniformity results in more overall uniform flux with respect to all types of filters and tighter controls with respect to molecular cutoffs in dialyzer applications.

Detailed Description Text (220):
Fiber membranes prepared by the method recited in Example 22 had sieving coefficients of 0.0 for albumin, 0.82 for myoglobin and 1.0 for inulin. These fibers had the surprising advantage of having high sieving coefficients for middle molecules (molecular weights of from about 5,000 daltons to 25,000 daltons) such as .beta..sub.2 microglobulins and myoglobins.

Detailed Description Text (224):
Resultant fiber membranes had sieving coefficients of 0.0 for albumin, 0.79 for myoglobin, and 1.0 for inulin.

Other Reference Publication (5):
Cabasso, "Hollow Fiber Membranes". Kirk-Othmer Encyclopedia & Chemical Technology, 3rd edition, John Wiley & Sons (editor: Martin Grayson). 12:492-517 (1984).

Other Reference Publication (6):
Wijmans et al., "The Mechanism of Formation of Microporous or Skinned Membranes Produced by Immersion Precipitation", Journal of Membrane Science, 14:263-274 (1983).

Other Reference Publication (10):
Uragami et al., "Studies on Synthesis and Pereability of Special Polymer Membranes", Polymer-Bulletin, 4:617-622 (Spring 1981).

Other Reference Publication (12):
V. Chen et al., "The use of anionic surfactants for reducing fouling of ultrafiltration membranses: their effects and optimization," Journel of Membrane Science, vol. 67, Nos. 2/3, 20, Mar. 1992.

CLAIMS:

20. A process for the manufacture of an improved microporous hollow fiber membrane having improved flux and rewetting characteristics, the process comprising:

38. A process for the manufacture of an improved microporous hollow fiber membrane having improved flux and rewetting characteristics, the process comprising:

53. A process for the manufacture of an improved microporous hollow fiber membrane having improved flux and rewetting characteristics, the process comprising:

89. An asymmetrical, microporous, hollow fiber membrane produced according to the process of claim 70 wherein said fibers exhibit sufficient strength to withstand take-up rates of about 75 m/min or greater.